

Fingerprints of Spin-Orbital Physics in Crystalline O₂

I. V. Solovyev*

Computational Materials Science Center, National Institute for Materials Science,
1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

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The alkali hyperoxide KO₂ is a molecular analog of strongly-correlated systems, comprising of orbitally degenerate magnetic O₂⁻ ions. Using first-principles electronic structure calculations, we set up an effective spin-orbital model for the low-energy *molecular* orbitals and argue that many anomalous properties of KO₂ replicate the status of its orbital system in various temperature regimes.

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Magnetic substances without *d*- or *f*-elements are exotic. Several rare examples include *sp*-impurities in alkali-metal hosts [1], CaB₆ [2], nonstoichiometric CaO [3], as well as some carbon-based materials [4]. Besides them, the solid oxygen is an absolutely unique magnetic system. This is because O₂ is the only elementary molecule, whose ground state is different from the conventional spin singlet. Therefore, if these molecules form a crystal (either by cooling or by pressurizing), it may become magnetic. In fact, the antiferromagnetism of solid O₂ is well known [5, 6, 7], and can be anticipated from the electronic structure of the single O₂ molecule, having two unpaired electrons in a doubly-degenerate π_g shell [6].

Since O₂ is a good oxidizer and can easily take an additional electron when it brought in contact with alkali elements, there is another way of making the crystalline O₂, in a form of ionic crystals (called “alkali hyperoxides”), which are similar to NaCl, but distorted due to elastic interactions involving O₂ molecules. One typical example is KO₂, which around the room temperature forms the body-centered tetragonal (bct) lattice (Fig. 1) [8, 9]. The uniqueness of this situation is that O₂ has an extra electron residing in the doubly-degenerate π_g shell, and KO₂ is the first molecular crystal, where the magnetism not only exists, but interplays with the orbital degrees of freedom, like in famous KCuF₃ [10] and LaMnO₃ [10, 11]. Typically, such materials are known for their rich magnetic properties, which depend on the orbital state.

This is clearly the case also for KO₂. The Curie-Weiss temperature (T_{CW}), extracted from the behavior of magnetic susceptibility (χ_m) in two paramagnetic regions changes the sign at around 200 K [8], indicating at the change of character of intermolecular interactions, from antiferromagnetic (AFM) to ferromagnetic (FM) with decrease of the temperature (T). The role of the crystal distortion in this region is somewhat controversial. On the one hand, there are some indications that the actual symmetry is lower than bct [8, 9]. On the other hand, no profound change of the magnetic behavior has been observed. For example, a sizable orbital contribution to the magnetization persists down to 13 K. Therefore, even if exists, the crystal distortion does not seem to fully control the magnetic behavior of KO₂ in the paramagnetic region. If so, what causes the change of T_{CW} ? Another interesting point is that below 13 K the situation is completely different and the behavior of KO₂ is strongly affected by frozen-in rotations of O₂ molecules, which quench the orbital magnetization and stabilize an AFM order. Nevertheless, the transition temperature is surprisingly low. Moreover, the AFM order can be broken up by a magnetic field. The transition is accompanied by structural changes, and the effect is called “magneto-gyration” [12].

The purpose of this work is to establish a theoretical basis for understanding the fascinating magnetic properties of KO₂ and other alkali hyperoxides. Using first-principles electronic structure calculations, we set up an effective spin-orbital model for the low-energy molecular states. Then, we show that the magnetic phase diagram of KO₂ replicates the status of its orbital system, which evolves (under heating) from a quenched state, to a region of relativistic spin-orbital correlations, and finally to the region of independent spin and orbital disorder.

The O₂ molecule appears to be the building block not only of the crystal, but also of the electronic structure of KO₂. The hybridization within a single molecule is so strong that it leads to the splitting and formation of quite distinguishable molecular levels. The interaction between molecules is considerably weaker, so that the molecular orbitals form a group of narrow nonoverlapping bands (Fig. 1, we use the experimental lattice param-

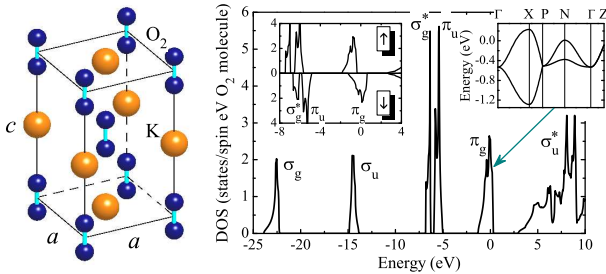


FIG. 1: (Color online) Tetragonal phase of KO₂ (left) and electronic structure in LDA (right). Left inset shows results of spin-polarized calculations. Right inset shows the π_g bands near the Fermi level (located at zero energy).

ters reported in Ref. [9]). Thus, there is a clear analogy with atomic limit in the theory of strongly-correlated systems [10], except that now the *molecular orbitals* play the same role as atomic orbitals in a conventional case.

According to electronic structure calculations in the local-(spin)-density approximation [L(S)DA], the doubly-degenerate π_g band located near the Fermi level is formed by antibonding molecular p_x and p_y orbitals (Fig. 1) [13]. The π_g bandwidth is comparable with the exchange spin-splitting ($\Delta_{\text{ex}} \sim 1$ eV). Hence, the system is half-metallic, and its magnetic properties can be understood in terms of FM double exchange (D) and AFM superexchange (S) interactions, which can be expressed through the first and second moments of occupied density of states for the \downarrow -spin π_g band as $J^D = -m^{(1)}/2z$ and $J^S = -m^{(2)}/z\Delta_{\text{ex}}$, where z is the coordination number [11]. Then, the Curie temperature will also consist of two parts, $T_C = T_C^D + T_C^S$, which can be evaluated in the mean-field approximation [14]. This yields $T_C^D = -4m^{(1)}/15k_B \approx 882$ K and $T_C^S = -m^{(2)}/3k_B\Delta_{\text{ex}} \approx -558$ K. Thus, $T_C \approx 324$ K, and KO_2 is expected to be a good ferromagnet, being in straight contrast with the experimental data. The root of the problem is the Coulomb correlations in the narrow π_g band, which are greatly oversimplified in LSDA.

In order to treat these effects rigorously, we derive an effective Hubbard-type model for the π_g band, starting from the LDA band structure:

$$\mathcal{H} = \sum_{ij} \sum_{\alpha\beta} h_{ij}^{\alpha\beta} c_{i\alpha}^\dagger c_{j\beta} + \sum_i \sum_{\alpha\beta\gamma\delta} U_{\alpha\beta\gamma\delta} c_{i\alpha}^\dagger c_{i\beta}^\dagger c_{i\gamma} c_{i\delta}. \quad (1)$$

The method has been explained in details in Ref. [15]. The basic difference here is that each lattice-point (i or j) corresponds to an O_2 molecule (rather than to a single atomic site). Each Greek symbol stands for a combination (m, s) of orbital ($m = p_x$ or p_y) and spin ($s = \uparrow$ or \downarrow) indices. Each orbital index refers to the *antibonding molecular p -orbital* of either x ($m=1$) or y ($m=2$) symmetry. The off-diagonal (with respect to i and j) elements of $h_{ij}^{\alpha\beta}$ stand for transfer integrals, which do not depend on spin indices: i.e., $\hat{h}_{ij} \equiv \|h_{ij}^{\alpha\beta}\| = \|t_{ij}^{mm'}\| \delta_{ss'}$ for any combination of $\alpha=(m, s)$ and $\beta=(m', s')$. They are derived from the LDA band structure using an *exact* version of the downfolding method [15, 16]. The results are summarized in Table I, up to fourth nearest neighbor. Other parameters are considerably smaller. The diagonal matrix elements, $h_{ii}^{\alpha\beta} = \langle \alpha | \xi \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} | \beta \rangle$, stand for the spin-orbit interaction (SOI) is a single molecule ($\xi \approx 34$ meV) and the crystal field, if the lattice distortion is applied.

The matrix of screened Coulomb interactions in the

π_g band has been computed in the two steps. First, we derive the interaction parameters between *atomic p -orbitals*, using the constraint-LDA method. It enable us to obtain the following parameters of intraatomic Coulomb interaction $u \approx 11.37$ eV, interatomic intramolecular Coulomb interaction $v \approx 2.52$ eV, and intraatomic exchange interaction $j \approx 2.30$ eV. Then, we

TABLE I: Transfer integrals and parameters of Heisenberg model (in meV) for undistorted bct phase. The nonequivalent vectors separating two O_2 molecules are denoted as $\mathbf{b}_1=(0, a, 0)$, $\mathbf{b}_2=(\frac{a}{2}, \frac{a}{2}, \frac{c}{2})$, $\mathbf{b}_3=(a, a, 0)$, and $\mathbf{b}_4=(0, 0, c)$. Other matrix elements $t_{ij}^{mm'}$ are obtained using symmetry operations and permutability of orbital indices, $t_{ij}^{12}=t_{ij}^{21}$.

| vector | t_{ij}^{11} | t_{ij}^{12} | t_{ij}^{22} | J_{ij}^{\parallel} | J_{ij}^{\perp} | \bar{J}_{ij} |
|----------------|---------------|---------------|---------------|----------------------|------------------|----------------|
| \mathbf{b}_1 | -1 | 0 | 106 | -0.44 | -1.09 | -0.47 |
| \mathbf{b}_2 | -51 | -98 | -51 | 1.13 | -1.03 | -1.03 |
| \mathbf{b}_3 | -11 | -11 | -11 | -0.02 | -0.04 | -0.02 |
| \mathbf{b}_4 | -13 | 0 | -13 | -0.06 | -0.06 | -0.01 |

take into account the screening of Coulomb interactions between p -orbitals in the π_g band by other bands, which are constructed from the same p -orbitals (i.e., the π_u band, which is the bonding combination of p_x - and p_y -orbitals, as well as the σ_g^* and σ_u^* bands, which have a strong weight of p_z -orbitals). This part is done in the random-phase approximation, which starts with interaction parameters obtained in constraint-LDA. Then, we are able to derive the interaction parameters between *molecular p -orbitals* in the π_g band: the intraorbital Coulomb interaction $U \approx 3.66$ eV and the exchange interaction $J \approx 0.62$ eV. The interorbital Coulomb interaction U' is related with U and J by the identity $U' = U - 2J$. These parameters define the whole matrix $\tilde{U} = \|U_{\alpha\beta\gamma\delta}\|$ of screened Coulomb interactions in the π_g band.

Since any of $t_{ij}^{mm'}$ is smaller than U by at least one order of magnitude, all transfer integrals can be treated as a perturbation, starting with isolated molecular orbitals. Then, it is convenient to use the *hole representation*. The advantage is that there is only one hole state associated with each molecular site. Therefore, if molecules were fully isolated, the holes would not interact with each other, and the ground state would be a single Slater determinant. By denoting the hole-orbitals associated with i and j as α_i and α_j , and constructing the two-hole determinant $G(\alpha_i, \alpha_j) = \frac{1}{\sqrt{2}} \{ \alpha_i(1)\alpha_j(2) - \alpha_j(1)\alpha_i(2) \}$, one can find the energy gain caused by virtual hoppings in each bond [17, 18]:

$$\mathcal{T}(\alpha_i, \alpha_j) = - \left\langle G(\alpha_i, \alpha_j) \left| \hat{h}_{ij} \left(\sum_M \frac{\hat{P}_j |jM\rangle \langle jM| \hat{P}_j}{E_{jM}} \right) \hat{h}_{ji} + (i \leftrightarrow j) \right| G(\alpha_i, \alpha_j) \right\rangle, \quad (2)$$

where E_{jM} and $|jM\rangle$ stand for eigenvalues and eigenstates of excited two-hole configurations at the site j , and \hat{P}_j is a projector operator, which enforces the Pauli principle and prevent any hoppings onto α_j [17]. Eq. (2) incorporates some intramolecular correlations beyond the Hartree-Fock approximation, which are included into the multiplet structure of the excited states.

First, we discuss the properties of the bct phase of KO_2 in an intermediate-temperature region, where the crystal distortion is small and $k_B T \ll \xi$ (note that $\xi/k_B \approx 395$ K), so that the splitting of the molecular π_g levels is largely controlled by the SOI, which provides the natural basis for the hole orbitals $\{\alpha_i\}$. In this case, each $|\alpha_i\rangle$ can be presented as a linear combination of only two orbitals, $|p_+\rangle$ and $|p_-\rangle$, which are split off by the SOI, and where $|p_\pm\rangle = \mp \frac{1}{\sqrt{2}}(|p_x\rangle \pm i|p_y\rangle)$ are the complex harmonics. Now, the spin and orbital variables are rigidly bound, and the problem can be reformulated in terms of the *pseudospin* states: $|\tau_x^\pm\rangle = \frac{1}{\sqrt{2}}(|p_+\rangle \pm |p_-\rangle)$, $|\tau_y^\pm\rangle = \frac{1}{\sqrt{2}}(|p_+\rangle \pm i|p_-\rangle)$, $|\tau_z^+\rangle = |p_+\rangle$, and $|\tau_z^-\rangle = |p_-\rangle$, which allow us to make a formal mapping of energies (2) onto the *anisotropic* Heisenberg model for the bct lattice and the pseudospin 1/2:

$$\hat{H} = -\frac{1}{2} \sum_{ij} \left\{ (\hat{\tau}_{ix} \hat{\tau}_{jx} + \hat{\tau}_{iy} \hat{\tau}_{jy}) J_{ij}^\perp + \hat{\tau}_{iz} \hat{\tau}_{jz} J_{ij}^\parallel \right\},$$

where $\hat{\tau}_x$, $\hat{\tau}_y$, and $\hat{\tau}_z$ are the 2×2 Pauli matrices in the basis of $|p_+\rangle$ and $|p_-\rangle$ orbitals. The parameters, calculated as $2J_{ij}^\perp = \mathcal{T}(\tau_{ix}^+, \tau_{jx}^-) - \mathcal{T}(\tau_{ix}^+, \tau_{jx}^+) = \mathcal{T}(\tau_{iy}^+, \tau_{jy}^-) - \mathcal{T}(\tau_{iy}^+, \tau_{jy}^+)$ and $2J_{ij}^\parallel = \mathcal{T}(\tau_{iz}^+, \tau_{jz}^-) - \mathcal{T}(\tau_{iz}^+, \tau_{jz}^+)$, are summarized in Table I. The direct exchange interactions between O_2 molecules are considerably weaker and can be neglected [5]. The interlayer coupling J^\parallel operating between neighboring molecules separated by \mathbf{b}_2 stabilizes the FM ground state. Hence, the pseudospin moments are parallel to the z axis. Other interactions are antiferromagnetic and frustrated on the bct lattice. The expectation values of the magnetic moments are given by the following identities: $\langle \tau_x^\pm | \hat{L}_x + 2\hat{S}_x | \tau_x^\pm \rangle = \langle \tau_y^\pm | \hat{L}_y + 2\hat{S}_y | \tau_y^\pm \rangle = 0$ and $\langle \tau_z^\pm | \hat{L}_z + 2\hat{S}_z | \tau_z^\pm \rangle = \pm 2$: i.e., the finite magnetization is allowed only along the z -axis, while it is totally quenched in the perpendicular (x and y) directions. The same matrix elements define the g -tensor (e.g., in χ_m).

Then, the magnetic properties can be easily calculated using renormalized spin-wave (SW) theory [19]. The idea is to extend the conventional formalism to finite temperatures by replacing in the expression for the SW frequency the value of local magnetic moment (in our case, the pseudospin moment) by its thermal average $\langle \hat{\tau}_z \rangle$: $\omega_{\mathbf{q}} = 2\langle \hat{\tau}_z \rangle (J_0^\parallel - J_{\mathbf{q}}^\perp) + 2b$, where $J_0^\parallel = \sum_j J_{ij}^\parallel$ and $J_{\mathbf{q}}^\perp$ is the Fourier transform of $\{J_{ij}^\perp\}$. On the other hand, $\langle \hat{\tau}_z \rangle$ is expressed through the averaged number of excited spin-waves, yielding the equation $\langle \hat{\tau}_z \rangle \sum_{\mathbf{k}} \coth \omega_{\mathbf{k}} / 2k_B T = 1$,

which is solved self-consistently for each T and the external field b , acting on $\hat{\tau}_z$. The expression for the Curie temperature, $(k_B T_C)^{-1} = \sum_{\mathbf{q}} (J_0^\parallel - J_{\mathbf{q}}^\perp)^{-1}$, can be derived by assuming $b = \langle \hat{\tau}_z \rangle = 0$ or from the divergence of $\chi_m = 4\mu_B^2 \langle \hat{\tau}_z \rangle / b$. The spectrum of SW excitations itself is rather remarkable (Fig. 2). All excitations are gapped. The gap in the Brillouin zone center is proportional to ξ , which is large on the temperature scale. However, all low-energy excitations correspond to the zone boundary, where $\omega_{\mathbf{q}}$ is largely reduced by AFM interactions J_{ij}^\perp . Thus, the FM order is expected only at $T_C \approx 66$ K, which is largely reduced in comparison with ξ/k_B (and, apparently, can be further reduced by small lattice distortions, which are seen in KO_2 [8, 9]). The renormalizes SW theory also predicts some small deviation from the Curie-Weiss law in the paramagnetic region, and the effective moment (μ_{eff}), derived from the slope of χ_m^{-1} , will generally depend on T . Indeed, μ_{eff} varies from $2\mu_B$ at large T till $2.17\mu_B$ near T_C . This may help to explain some deviations of μ_{eff} from its nominal value [8].

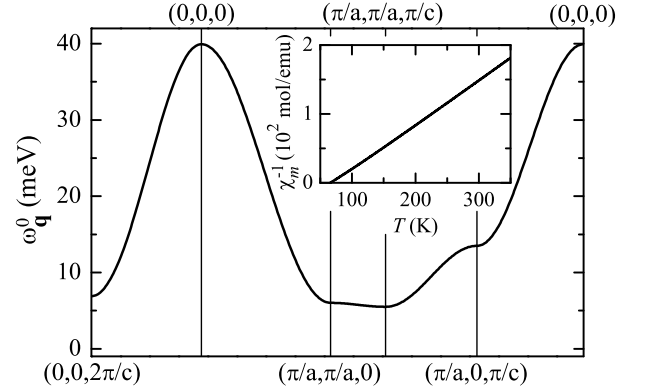


FIG. 2: The unrenormalized spin-wave dispersion of anisotropic Heisenberg model: $\omega_{\mathbf{q}}^0 = 2(J_0^\parallel - J_{\mathbf{q}}^\perp)$. The inset shows the inverse magnetic susceptibility in the paramagnetic region, as obtained in the renormalized spin-wave theory.

In the high-temperature region, $k_B T \gtrsim \xi$, the thermal fluctuations will eventually destroy the coupling between spin and orbital degrees of freedom, which now can be treated as independent variables. Then, the *spin* Hamiltonian can be derived by averaging the pair interactions (2) over *orbital* variables [10]. Practically, for each projection of spin, one can consider the whole family of possible hole-orbitals, $|\alpha_i^{\uparrow, \downarrow}\rangle = \cos \theta_i |p_x \uparrow, \downarrow\rangle + \sin \theta_i e^{i\phi_i} |p_y \uparrow, \downarrow\rangle$ (where $0 \leq \theta_i \leq \pi$ and $0 \leq \phi_i \leq 2\pi$), and to average (numerically) each $\mathcal{T}(\alpha_i^{\uparrow, \downarrow}, \alpha_j^{\uparrow, \downarrow})$ over all combinations of (θ_i, ϕ_i) and (θ_j, ϕ_j) . The simplest approximation, which is justified for large T , is to assume that all combinations are equivalent and to neglect the spacial correlations between orbitals. Obviously, the spin system will be isotropic, and the parameters of Heisenberg model can be found as $2\bar{J}_{ij} = \bar{\mathcal{T}}_{ij}^{\uparrow\downarrow} - \bar{\mathcal{T}}_{ij}^{\uparrow\uparrow}$, where $\bar{\mathcal{T}}_{ij}^{\uparrow\downarrow}$ and $\bar{\mathcal{T}}_{ij}^{\uparrow\uparrow}$ are the averaged values of $\mathcal{T}(\alpha_i^{\uparrow}, \alpha_j^{\downarrow})$ and $\mathcal{T}(\alpha_i^{\uparrow}, \alpha_j^{\uparrow})$, respectively. All param-

eters are antiferromagnetic (Table I), which naturally explain the sign of T_{CW} in the high-temperature region [8]. The absolute value of T_{CW} can be estimated from the behavior of spin susceptibility (χ_s), in the framework of renormalized SW theory. Note that χ_s alone should provide a good estimate for the total χ_m in the perpendicular xy -plane, where the orbital magnetization is quenched. This yields $T_{CW} \approx -100$ K, which was derived from the linear interpolation of χ_s^{-1} at large T .

Thus, the existence of several paramagnetic segments with different T_{CW} 's can be related with a gradual increase of on-site correlations between spin and orbital degrees of freedom, driven by the SOI in the *bct* phase. In the high-temperature region, the spin and orbital variable are totally decoupled, that explains the AFM character of intermolecular interactions. On the other hand, the strong spin-orbital correlations in the intermediate-temperature regime would lead to a ferromagnetism.

The crystal distortion plays a sizable role only at very low T , as it is clearly manifested in the quenching of orbital moments and the observed AFM order [8]. Although exact details of the low-temperature structure are unknown, a number of experimental data speak in favor of uniform rotations of O_2 molecules around one of tetragonal axes as the main distortion. Certainly, such a distortion will lift the degeneracy of molecular p_x and p_y levels, and lead to a FM orbital order, which typically coexists with AFM correlations between the spins [10]. However, the situation is not so simple. Let us consider a distorted structure, which was obtained by the rigid clockwise rotation of O_2 molecules around the y -axis by 30° (the experimental value [8, 9]) in the fixed tetragonal frame, and derive parameters of the model Hamiltonian (1) for the (deformed) π_g band. The obtained “crystal-field splitting” of molecular π_g levels is about 290 meV, which exceeds ξ by nearly one order of magnitude and stabilizes the p_y -orbital (opposite to the assumption made in the phenomenological theory of magnetogyration [12]). Generally, the transfer integrals are specified by all three parameters (t^{11}, t^{12}, t^{22}) [20]. For the neighboring O_2 molecules, they are $(-20, 0, 74)$, $(-25, 0, 2)$, $(37, -29, -67)$, and $(-43, 35, -21)$ meV, for $\mathbf{b}_1 = (0, a, 0)$, $\mathbf{b}_1^* = (a, 0, 0)$, $\mathbf{b}_2 = (\frac{a}{2}, \frac{a}{2}, \frac{c}{2})$, and $\mathbf{b}_2^* = (-\frac{a}{2}, \frac{a}{2}, \frac{c}{2})$, respectively. Thus, the transfer integrals are strongly anisotropic, both in and between the tetragonal xy -planes. Since the SOI is no longer important, the energies (2) can be mapped onto rotationally invariant ($J_{ij}^\perp = J_{ij}^\parallel$) Heisenberg model. The natural choice of the hole orbitals, $|p_y \uparrow\rangle$ or $|p_y \downarrow\rangle$, is dictated by the crystal-field splitting. This yields the following interaction parameters $J_{ij} = -0.77, 0, -0.59, 4, -0.09$, and -0.01 meV between O_2 molecules separated by the vectors $\mathbf{b}_1, \mathbf{b}_1^*, \mathbf{b}_2, \mathbf{b}_2^*, \mathbf{b}_3$, and \mathbf{b}_4 , respectively. They form quasi-two-dimensional networks, where interactions in the planes perpendicular to $[\mathbf{b}_1 \times \mathbf{b}_2]$ are much stronger than those between the planes. This suppresses any long-range mag-

netic order [21]. Moreover, the AFM interactions in each plane are frustrated. Therefore, the Néel temperature (T_Q) is expected to be small. Indeed, from the mean-field analysis of the Heisenberg model we conclude that the ground state is a (nearly AFM) spin-spiral with $\mathbf{Q} \approx (0, \frac{3.77}{a}, \frac{0.02}{c})$. Then, the renormalized SW theory yields $T_Q \approx 11$ K, being in good agreement with the experiment [8]. The first-order transition to the FM *bct* phase in a magnetic field is also anticipated.

In summary, KO_2 is the new molecular analog of correlated spin-orbital systems. The geometry of *molecular* orbitals adds new functionalities into this classical problem. There is also a number of open questions. Particularly, any quantitative theory of magnetogyration is missing. Why do the O_2 molecules tend to rotate at low T ? Why do their orientation is different in KO_2 and NaO_2 ? These problems prompt further research.

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* Electronic address: solovyev.igor@nims.go.jp

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